Survey of TOC analytical methodologies used by State Water Project Contractors

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Background

Total organic carbon (TOC) is an important constituent in drinking water. TOC is a precursor of disinfection by-products (DBPs) which are considered to be potential carcinogens. Disinfection byproducts are formed when disinfectants used in water treatment plants react with bromide and/or natural organic matter present in the source water. Different disinfectants produce different types or amounts of disinfection byproducts. Disinfection byproducts for which regulations have been established include trihalomethanes (THMs), haloacetic acids (HAA5), bromate, and chlorite. In December 2001, EPA's Disinfectants/Disinfection Byproducts Rule (D/DBPR) will lower the Maximum Contaminant Level (MCL) for total THMs from 100 ppb to 80 ppb (annual average). The new MCLs for the other DBPs will be 60 ppb for HAA5, 10 ppb for bromate and 1 ppm for chlorite.

There is no MCL for TOC in drinking source water. However, the D/DBPR will require water treatment plants to implement coagulation/precipitation depending on a combination of TOC concentration and alkalinity in their source water. The trigger to implement coagulation will be a TOC of greater than 2 ppm. Plants meeting alternative compliance criteria in the Rule may be exempted.

There are several recognized methods for determining TOC concentration. However the approved methods by the California Department of Health Services (CDHS) Environmental Laboratory Accreditation Program (ELAP) for drinking water are the EPA 415.1 and the equivalent Standard Methods 5310 B, C and D. The methods can be conducted either by combustion (EPA 415.1, Standard Methods 5310 B) or oxidation (EPA 415.1, Standard Methods 5310 C and D). There has been concern that the two approaches do not generate comparable data. Until November 2000, DWR had used the oxidation (EPA 415.1) in analyzing SWP source water. Method comparisons indicated that the oxidation method was reporting significantly lower TOC levels than combustion especially at higher TOC levels. DWR then switched to the combustion method. DWR is undertaking a further study to gather information that will provide guidance on method selection in the future. The study is in three phases:

1. Survey the SWP Contractors to determine the prevalent approach for TOC analysis.
2. Perform a literature review of factors that may cause the observed differences in analytical results and their potential impacts on treatment plant DBP compliance.
3. Conduct method comparison using different source water matrices across seasons.

DWR has concluded the first phase of this project, and a summary of the results follow.

Phone survey of SWP water treatment plants (WTPs)

The main phone survey was conducted on September 13th, 14th, and 17th, 2001 by DWR staff. Follow up calls were made during the rest of September to facilities that could not be reached in the initial stage and also to WTPs where further clarifications were needed. The purpose of the survey was to determine whether there was a prevalent methodology for analyzing TOC in drinking source water among the SWP Contractors. Additional information such as rationale for selecting the particular method, range of TOC concentrations encountered in the source water, instrumentation used, etc was obtained wherever possible. The general response to the phone survey was positive and the facility contacts were very cooperative.

Most but not all SWP Contractors have drinking water treatment plants. 41 water treatment plants (WTPs) operated by SWP Contractors were contacted, Table 1. Some Contractors operate multiple treatment plants.

Table 1. SWP facilities surveyed for TOC analysis

Number of WTPs surveyed	Number of labs serving the surveyed WTPs	Number of labs that perform TOC analysis
41	26	25

Some Contractors depend on the SWP as their sole source while other Contractors blend their SWP allotment with supplies from other sources. The range of TOC concentrations encountered is therefore not necessarily representative of the SWP water quality. In most cases, the water treatment plant operator or laboratory supervisor was the designated facility contact.

Results

There are 26 analytical laboratories that perform water quality analyses for the 41 water treatment plants as shown in Table 1. Water treatment plants within the same water agency usually use the same lab for analysis. The majority of the labs are in-house. At the time of this survey, there were 19 in-house labs and 6 contract labs, Table 2. One agency has not been testing for TOC in their source water and so they could not provide TOC information.

Out of the 24 labs that perform TOC analysis which responded, 19 use the oxidation method, 3 use the combustion method, and one uses both methods (Table 2). One lab uses UVA and is only included for the sake of completeness. One lab did not respond to requests for information. Therefore, about three-quarters (76%) of the SWP analytical labs use UV/persulfate oxidation. The make and model of the instruments utilized varied. The most common makes were Shimadzu® and Tekmar-Dohrmann®. Other makes include Sievers®, Anatel®, Rosemont®, O.I.®, and Hach® (Table 2). TOC concentrations in the source waters ranged from 1 to 54 ppm but most were in the 2-5 ppm range. When queried about their plans for complying with the D/DBPR in 2002, facilities felt that it was not going to be a problem. None of the plants were making any special plans in terms of how they will analyze TOC in the future.

Although oxidation was the most prevalent approach among the labs, there were no identifiable explanations why the method was selected in the first place. The main explanation was that the lab had always used that particular approach. Most of the labs followed the Standard Methods 5310 C procedure, which is equivalent to the EPA 415.1 except for minor QC variations. The labs that had experience with combustion had varying opinions. Two labs have compared the two methods in the past. The first lab found the results from combustion to be too erratic when compared to the oxidation and decided to stay with the latter. The second lab performed comparisons of the two methods for a one-year period and found the results to be comparable with no significantly higher results from the combustion method. Their combustion instrument used a platinum catalyst and a 2-minute purge time and was more sensitive to lower TOC levels. A third lab uses the combustion method only but was not satisfied with the results and suggested increasing the purge time. The personnel at this lab consider the length of the purge time and the type of catalyst used to be important when evaluating the results of the combustion method.

Discussion

The oxidation method appears to be the most widely utilized approach among the SWP contractors. There did not appear to be any researched explanations why most of the labs favor this method except that it is what has always been performed. As far as it could be ascertained, there have not been documented studies at any of the facilities on how the method selected might affect compliance after the D/DBPR regulations come into effect in 2002.

Table 2. TOC analytical methodologies among the SWP treatment facilities

Lab #	**TOC Method**	**Instrument make**	**Laboratory type**	**Range of TOC** (ppm)
1	Oxidation	Anatel	In-house	Winter 20-54, summer 15-16
2	Oxidation	Tekmar Dohrmann Phoenix 8000	In-house	3-4
3	Oxidation	Shimadzu 4100	In-house	3-4
4	Oxidation	Tekmar Dohrmann DC-80	Contract	
5	Oxidation	Sievers 800	Contract	2-4
6	Oxidation	Rosemont DC-180	In-house	2.5-4.5
7	Oxidation	Tekmar Dohrmann Phoenix 8000	In-house	1-4
8	Oxidation	O.I. 700	In-house	1-5
9	Oxidation	Tekmar Dohrmann DC-180	In-house	2.6-16.4
10	Oxidation	Tekmar Dohrmann Phoenix 8000	In-house	4 -5
11	Oxidation	Hitachi 5000	In-house	2-3
12	Oxidation	Sievers 800	In-house	2-6
13	Oxidation	Tekmar Dohrmann Phoenix 8000	Contract	2.3-3.3
14	Oxidation	Tekmar Dohrmann Phoenix 8000	In-house	4-8
15	Oxidation	Tekmar Dohrmann DC-80	Contract	2-3
16	Oxidation	Shimadzu 5000A	In-house	4-5
17	Oxidation	--	Contract	5-22
18	Oxidation	Shimadzu 5000A	In-house	3.7-4.5
19	Oxidation	Tekmar Dohrmann Phoenix 8000	In-house	2.6 -5.1
20	Combustion	Shimadzu 5000	In-house	5 - 8
21	Combustion	Shimadzu 5000	In-house	2-4
22	Combustion	Shimadzu 5050	In-house	2-3
23	Combustion/oxidation	Tekmar DC-80/ Shimadzu	In-house	2
24	UVA 254	Hach DR 4000	In-house	4-20
25	No TOC analysis	N/A	N/A	N/A
26	Did not respond	?	Contract	?